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PHYSICS

INVESTIGATIONS ON THE EFFECT OF MANGANESE IONS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZNS NANOPARTICLES SYNTHESIZED BY SOLVO-THERMAL ROUTE

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Abstract

Nanoparticles of Zinc Sulfide (ZnS) doped with manganese ions (Mn^{2+}) with different ratios were synthesized by solvothermal route using a microwave oven. The X-ray diffraction patterns showed the typical interplanar spacings corresponding to the cubic phase. UV-visible optical spectroscopy study was carried out to determine the band gap energy of the nanocrystalline ZnS and ZnS:Mn particles. Variation of band gap energy with different ratios of Mn2+ was studied. ESR studies were carried out for the synthesized nanoparticles of this work and 'g' factor was determined. For morphological analysis, SEM studies for the prepared nanoparticles were performed. The chemical groups of the samples have been identified by FTIR studies. EDAX studies were carried out to identify the elements present in the samples.

Keywords: ZnS nanoparicles, XRD, microwave, electron spin resonance, SEM, EDAX, doped nanoparticle

Introduction

Semiconductor nanoparticles have tremendous applications due to their superior luminescence characteristics and high quantum efficiency. Among these materials, Zinc Sulfide (ZnS) is a II-VI group semiconductor with band gap energy of 3.7 eV at room temperature and it has received much attention due to its prominent applications in many fields [1]. As a well known luminescence material, ZnS shows various luminescence properties such as photoluminescence [2], electroluminescence [3] and mechanoluminescence [4]. Doped semiconductors of nanoparticles of dimensions below Bohr diameter exhibit interesting optoelectronic properties due to quantum size effect and are potential candidates for a variety of applications. ZnS nanoparticles doped with transition metal ions and rare earth ions have been successfully prepared by techniques such as thermal evaporation, sol-gel processing, co-precipitation, micro emulsions etc [5-10]. These doped ZnS semiconductor nanomaterials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, optical sensors etc. In this work, undoped and manganese-doped ZnS nanoparticles were synthesized by solvo-thermal route using a domestic microwave oven. Compared with conventional heating, microwave heating has an advantage of high efficiency and rapid formation of nanoparticles with a nano-size distribution and less agglomeration. The fundamental mechanism of microwave heating involves agitation of polar molecules or ions that oscillate under the effect of an oscillating electric field. In the presence of an oscillating field, particles try to orient themselves. This constant re-orientation creates friction and collisions between molecules, thus producing heat [11,12]. The aim of this paper is to report the results of investigations on the synthesis, X-ray diffraction (XRD) studies, UV-visible absorption studies, SEM studies, FTIR studies, EDAX studies and Electron Spin Resonance(EPR) studies of undoped and manganese-doped ZnS nanoparticles.

Experimental techniques

Synthesis

In order to synthesis undoped and ZnS:Mn nanoparticles by solvothermal route, zinc acetate dihydrate [$Zn(CH_3CO_2)_2.2H_2O$], manganese acetate dihydrate [$Mn(CH_3CO_2)_2.2H_2O$], thiourea (H_2NCSNH_2) were used as the precursors. Ethylene glycol was used as the solvent. Four different concentrations of manganese acetate viz. 1 mol %, 2 mol% , 3 mol% and 4 mol% were used as dopants in the preparation of ZnS:Mn compounds. To start with, the solutions containing zinc acetate, manganese acetate and thiourea in the proposed ratios were mixed well and the mixture solution was stirred well using a magnetic stirrer for about 1 hour. Then the mixed solution was

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placed in a bowl inside a domestic microwave oven (900 W, 2450 MHz., Onida, India) at a temperature of 80 ^{0}C. The solution was microwave treated until the solvent evaporates completely. After this, the substance deposited in the bowl was taken out, washed at least five times with double-distilled water. Then, the sample was washed with at least two times in acetone to remove any unwanted organic compounds present. Cleaning is necessary to remove the surface impurities and minimize particle agglomeration. The synthesized nanoparticles were filtered using a conical flask set up and the sample was dried in an oven at 60 ^{o}C .

Instrumentation

The crystalline structure, phase purity and size of the nanoparticles were determined by X-ray powder diffraction (XRD) technique. The XRD patterns were recorded with an automated X-ray powder diffractometer (PANalytical) with nickel filtered, monchromated CuKα radiation (λ= 1.54056 Å) at 35 KV, 10 mA. The samples were scanned over the required range for 2Θ values (10 – 70°). The morphology of the nanoparticles was examined by Scanning Electron Microscope (SEM) and the SEM images of the synthesized nanoparticles were recorded using a Hitachi Scanning Electron Microscope. Absorption spectra were recorded with a Varian Cary 1E UV-VIS spectrophotometer and this study was carried out at room temperature. ESR spectra for the samples were recorded using E112 Varian spectrometer. The Fourier Transform Infrared (FTIR) spectra of the samples were recorded using JASCO FI-IR 460 spectrometer by KBr pellet technique in the range 400-4000 cm^{-1} .

Results and Discussion

The samples in this work were synthesized in a domestic microwave oven. Microwave is electromagnetic radiation with frequency range of 0.3–300 GHz and corresponding wavelengths from 1 mm to 1 m. In the microwave irradiation region, the frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore rotation. However, the frequency is not high enough for the rotation to precisely follow the field, which causes energy to be lost from the dipole by molecular friction and collision, giving rise to dielectric heating. This method has been successfully applied for the preparation of a variety of nano-sized inorganic materials [13-15]. Compared with conventional heating, microwave heating has an advantage of high-efficiency and rapid formation of nanoparticles with a narrow size distribution and no serious agglomeration. When microwave oven is used to prepare the nanoparicles of this work, particles are observed to be spherical in shape and to be less agglomeration in the samples as seen in SEM images.

The X-ray diffraction (XRD) patterns of the undoped and manganese-doped ZnS nanoparticles (4 mol%) are presented in the figures 1 and 2. The indexing of the diffraction peaks has been carried out using the software INDEXING and the observed values for the peaks are (111), (220) and (311). The broadening of the peaks of the XRD patterns indicates that the samples consist of particles of nano-range. The size of particles was determined using Debye-Scherrer's relation $t = (0.9\ \lambda)/(\beta \cos \theta)$ where t is the particle size, λ is the wavelength of the X-rays, β is the Full Width at Half Maximum(FWHM)and θ is the Bragg's angle for the peak considered[16]. The average size of undoped and manganese-doped ZnS nanoparticles was found to be 6.31 nm and 5.80 nm respectively.

Figure 1: Powder XRD pattern for undoped ZnS nanoparticles

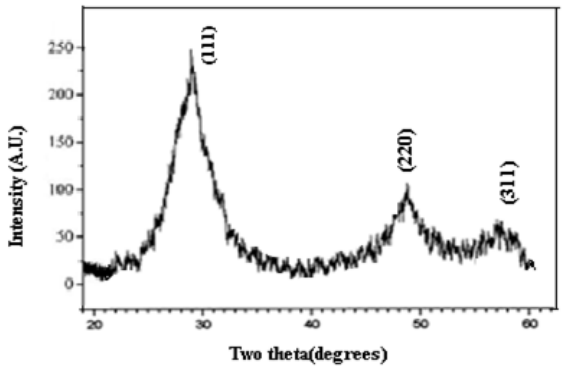
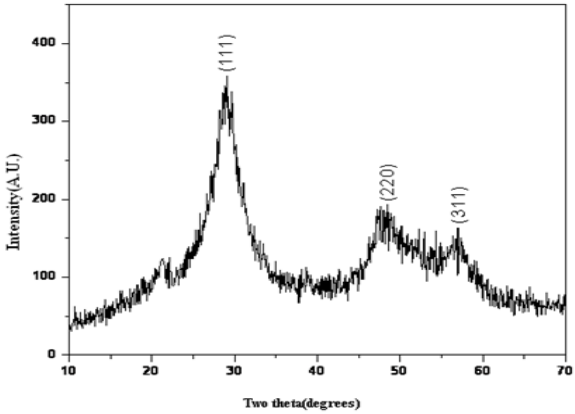
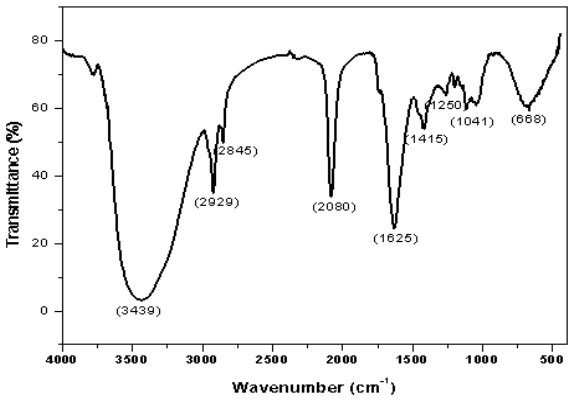


Figure 2: Powder XRD pattern for ZnS: Mn nanoparticles



The Fourier Transform Infrared (FTIR) spectrum of the undoped ZnS nanoparticles is shown in the figure 3. The broad peak in the higher energy region at 3439 cm^{-1} is due to OH stretching and the peak at 1625 cm^{-1} is due to OH bending of adsorbed moisture in the sample and all the other peaks are attributed to the characteristic of the material. Since FTIR spectra of the doped samples of this work are observed to be the similar patterns as that of undoped ZnS sample, the spectra are not provided here.

Figure 3: FTIR spectrum of undoped ZnS nanoparticles



Electron Spin Ressonce (ESR) spectra were recorded for different Mn concentration and are shown in figure 4. The yield sample quantity was 60 mg in each case. The ESR spectra observed for ZnS doped with 1 mol%, 2 mol%, 3 mol% and 4 mol% of Mn show one symmetric single line. The presence of single line suggests that the system is not completely diluted and the broadening of the line width can be explained by the dipolar coupling between Mn^{2+} ions in the host matrix of ZnS. The g-factor was calculated and is shown in the table 1. Using the formula g B H = h ν (where h is the Planck's constant, ν is the frequency of radiation used, g is the splitting factor, B is the electronic Bohr magneton and H is the strength of applied magnetic field), the g-factor was calculated.

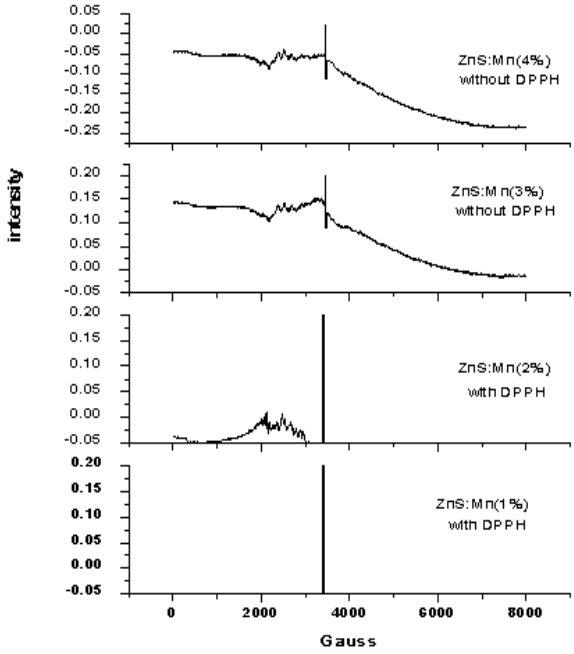


Figure 4: ESR patterns of ZnS:Mn (1%, 2%, 3%, 4%)

Table 1: The g-factor values for ZnS doped with 1%, 2%, 3% and 4% Mn

Compound	ν Microwave frequency (GHz)	H Field strength (gauss)	g- factor
ZnS:Mn(1%)	9.34	3410	1.9567
ZnS:Mn(2%)	9.36	3417	1.9569
ZnS:Mn(3%)	9.49	3454	1.9628
ZnS:Mn(4%)	9.49	3456	1.9617

The optical absorption spectra of manganese-doped ZnS nanocrystals are shown in the figure 5. The band gap energies of the samples were calculated using the α^2 vs hv graph shown in the figure 6. The band gap energies are 3.822 eV, 3.825 eV, 3.83 eV and 3.832 eV for ZnS nanocrystals doped with Mn 4%, 3%, 2% and 1% respectively. It is clear that the band gap energy decreases as the doping concentration of Mn is increased and thus shift is notice towards longer wavelengths.

Figure 5: UV-Vis absorption spectra for ZnS:Mn samples

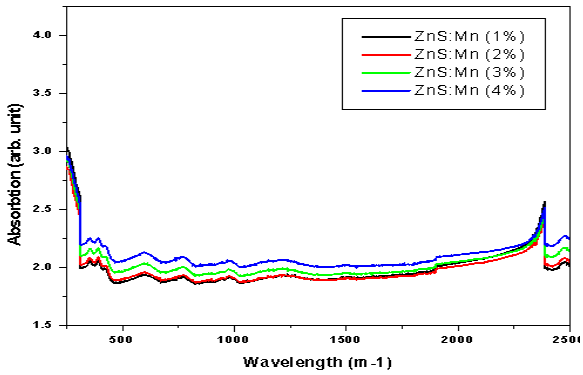
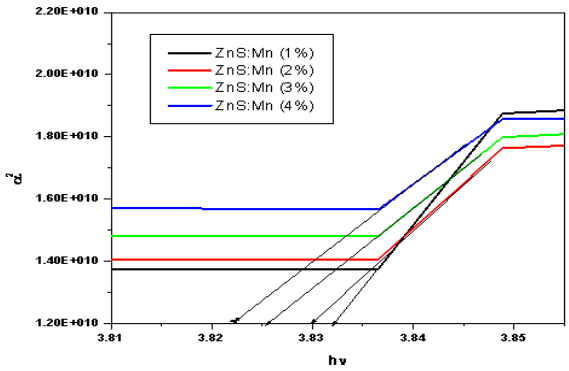


Figure 6: Variation of α2 with hv of the samples



The scaning electron microscopic (SEM) images of undoped and Mn-added ZnS nanoparticles are presented in the figures 7 and 8. It is observed from the SEM images that the samples consist of many round-shaped particles. The presence of elements in the sample ZnS is identified with the help of Energy dispersive X-ray Analysis (EDAX) spectrum given in the figure 9.

Fig.7: SEM image for undoped ZnS sample

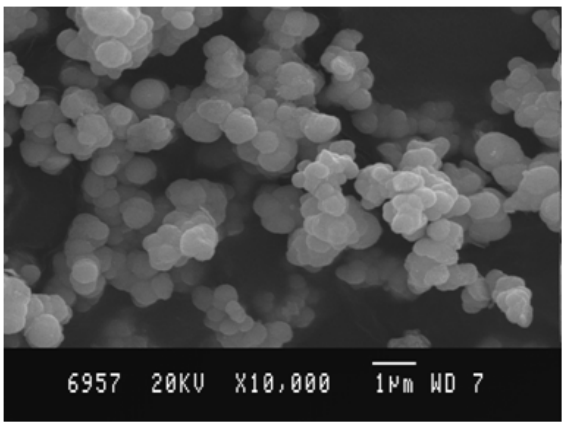


Fig.8: SEM image for manganese-doped ZnS sample (4 mol%)

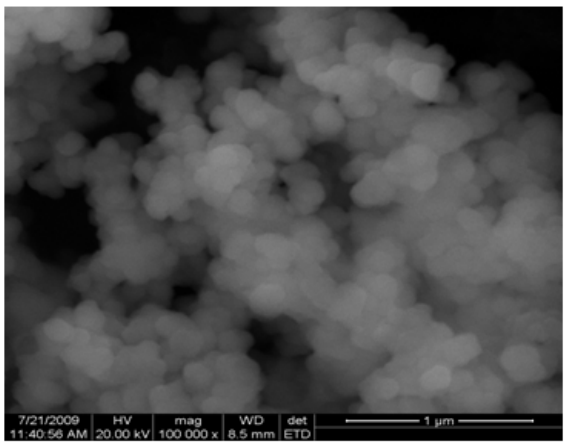
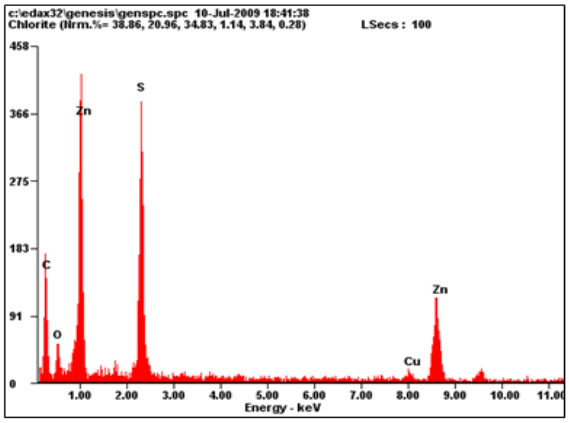


Fig.9: EDAX spectra for ZnS sample



Conclusion

Nanoparticles of undoped and manganese-doped ZnS been prepared by the solvothermal technique using a domestic microwave oven. The structure and phase purity of the samples were determined using X-ray diffraction method. The surface morphology of the as-prepared powders was observed from SEM studies and it is noticed that most of the particles are spherical in shape. The band gap energy of the materials was determined using optical absorption spectroscopic technique and band gap energy was found to be decreasing with increase in the concentration of dopant (manganese) in ZnS samples. The 'g' factor values were calculated from ESR spectra. The elements present in the sample were identified from EDAX spectra.

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